RDT&E for Emerging Contaminants

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Report Documentation Page

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DoD's Environmental Technology Programs

Science and Technology

Demonstration/ Validation

Environmental Drivers
Sustainability of Ranges, Facilities, and Operations

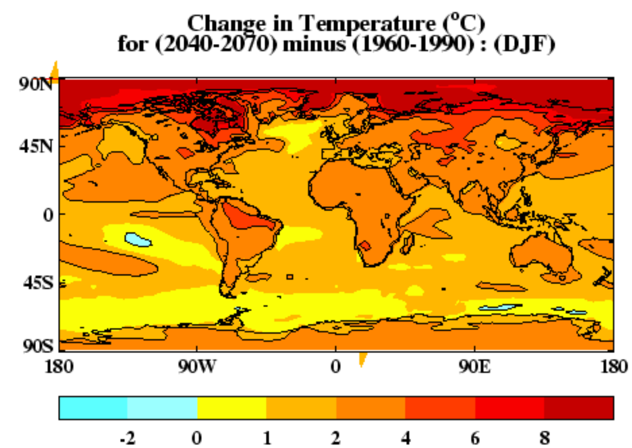

Maritime Sustainability
Threatened and Endangered Species


Toxic Air Emissions and Dust

UXO & Munitions Constituents

Noise

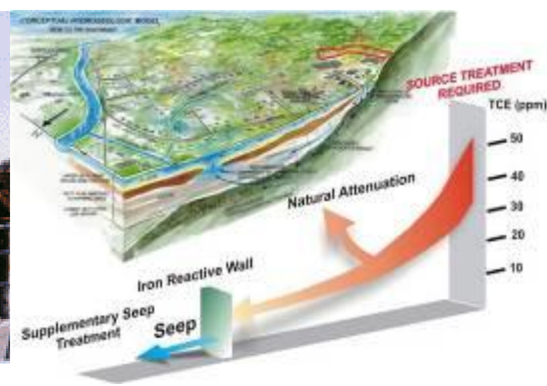
Urban Growth & Encroachment



Climate Change & GHG

Environmental Drivers
Reduction of Current and Future Liability

Contamination from Past Practices

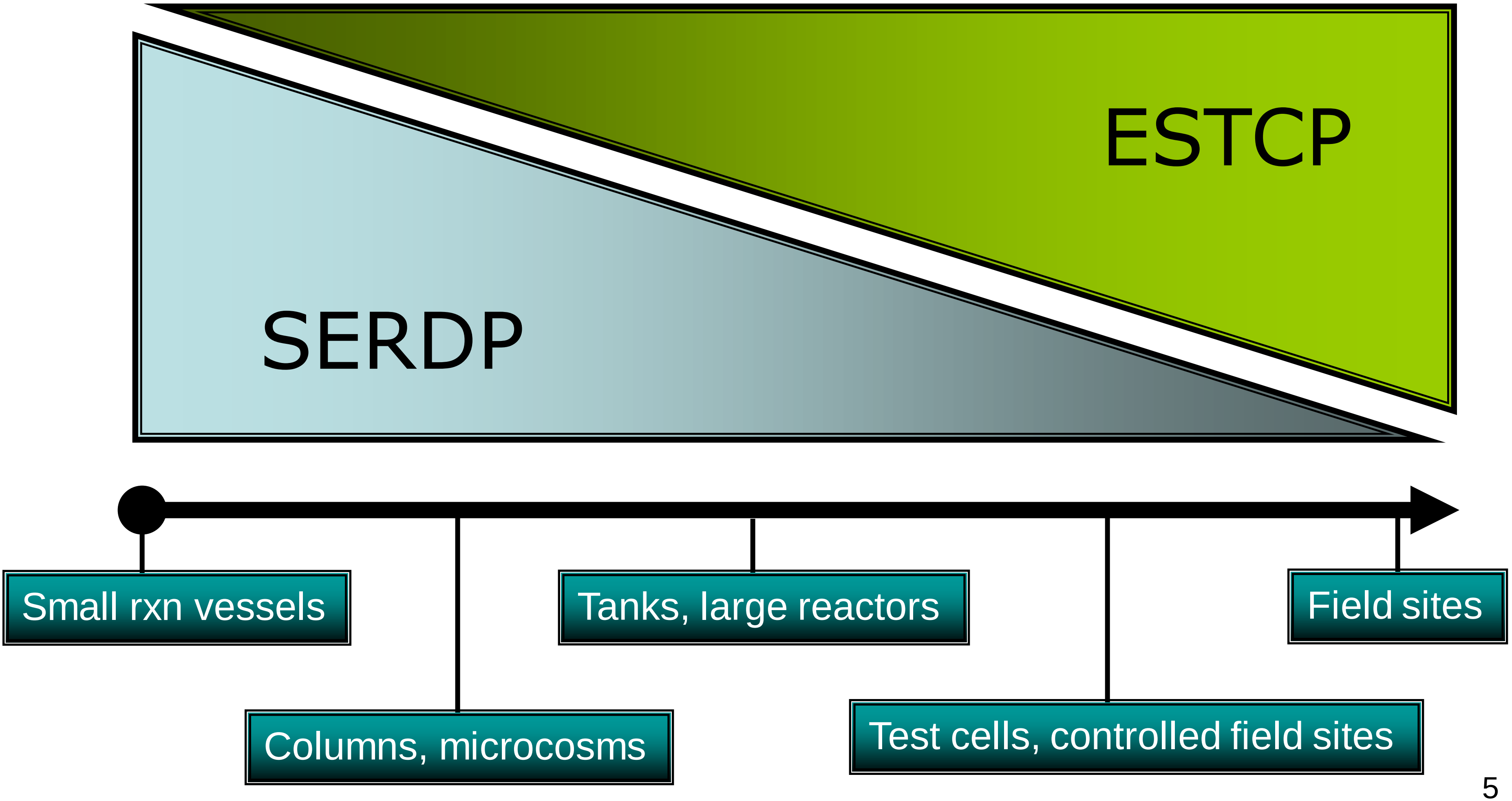


- Groundwater, Soils and Sediments
- Large UXO Liability
- Emerging Contaminants

Pollution Prevention to Control Life Cycle Costs

- Elimination of Pollutants and Hazardous Materials in Manufacturing Maintenance & Operations
- Achieve Compliance Through Pollution Prevention

Scales of Research



Emerging Contaminant Defined

- Synthetic or naturally-occurring chemical or microbe
- Not commonly monitored
- Potential to enter the environment and cause known or suspected adverse environmental or health effects
- Sometimes heretofore undetectable

From USGS website

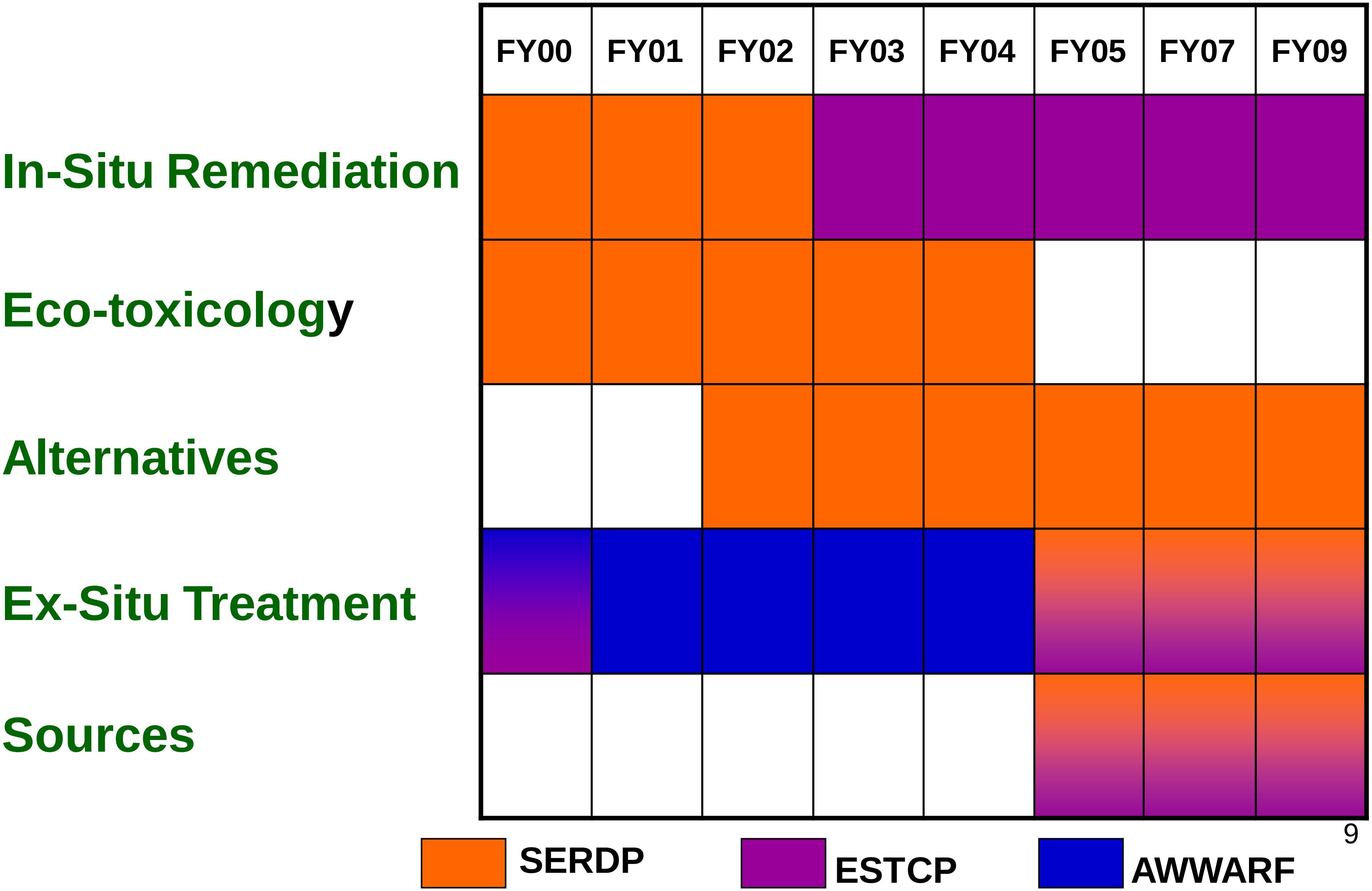
Current Research on Emerging Contaminants

- Perchlorate
- NDMA
- 1,4-Dioxane
- PFCs

Perchlorate Issue

- Broad Use & Occurrence
  - DoD
    - Rocket propellant
    - Insensitive munitions
  - Pyrotechnics and flares
  - Agricultural
  - Natural deposition

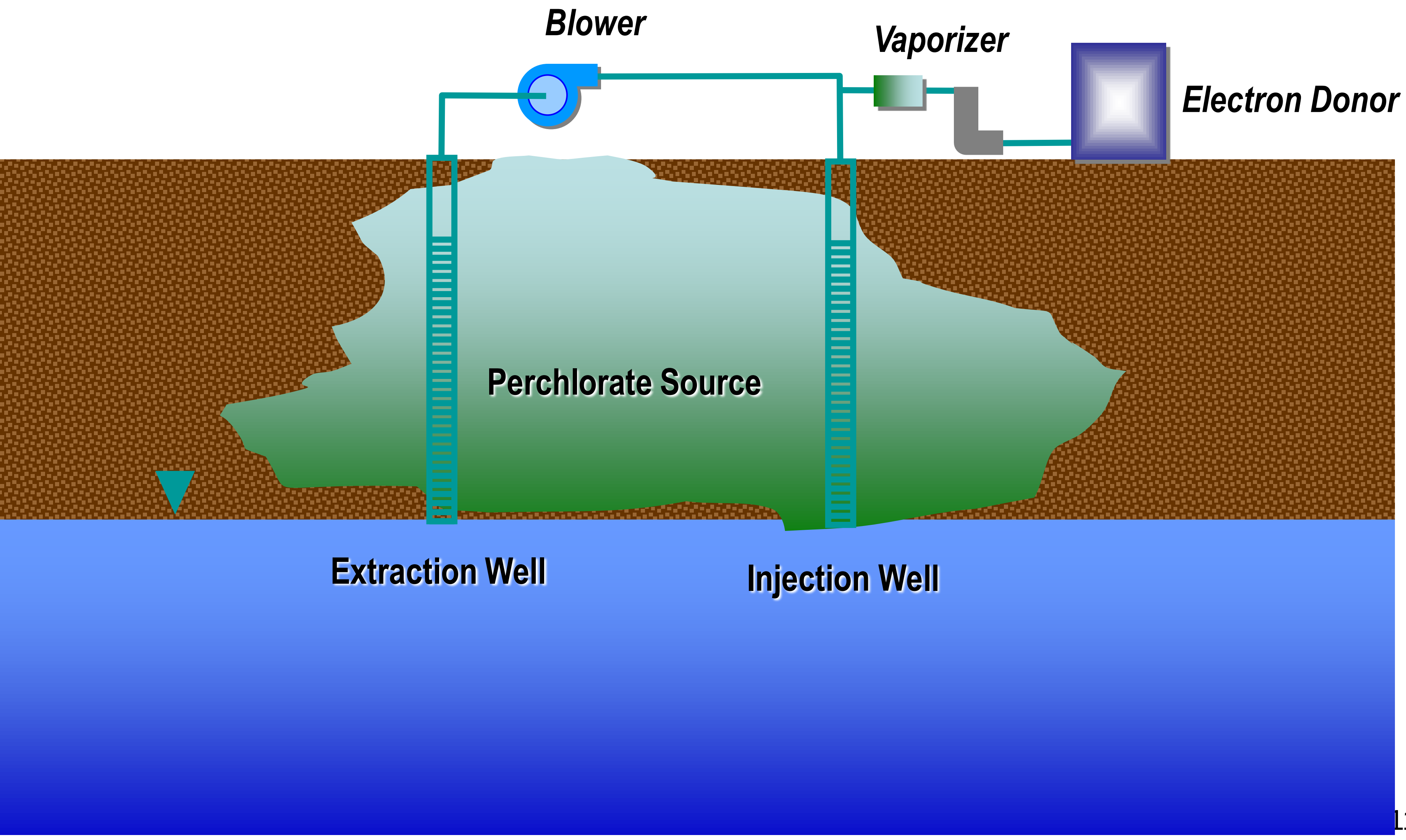
Perchlorate RDT&E



Eco-Toxicology

- SERDP initiated studies in 1998
- A comprehensive program
  - amphibians
  - fish
  - invertebrates
  - birds
  - small mammals
- Laboratory and field studies
- Work is the basis for EPA eco-risk assessment
- Investment Completed
- Comprehensive book being written

Vadose Zone Treatment



Ex Situ Treatment

- 1998 drinking water treatment R&D was initiated by an industry consortium (AWWARF)
  - Completed in 2004
- Successful ESTCP waste water bio-treatment transitioned in 2000
- Only ion-exchange currently used for drinking water
- FY2005 initiatives
  - ESTCP Congressional program to dem/val new approaches (ion exchange, biotreatment, tailored GAC)
  - SERDP develop program for next generation treatment

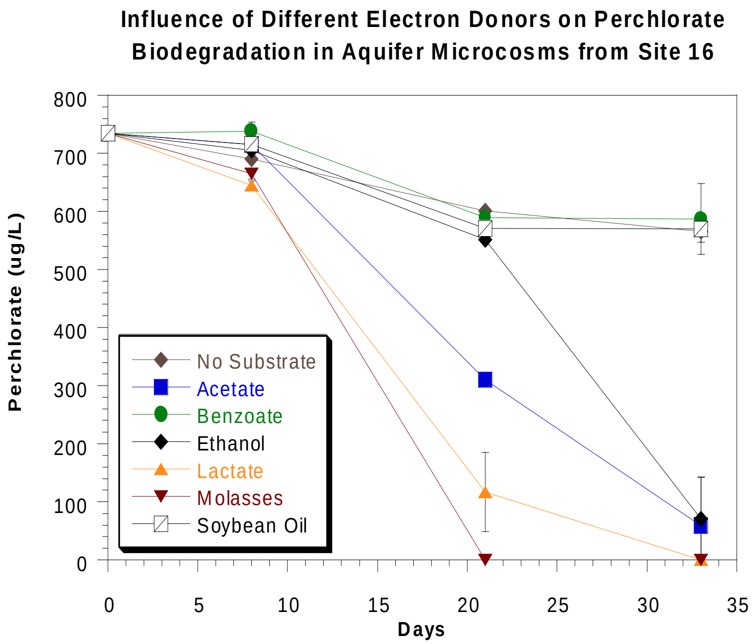
Ex-Situ Bio-Reactor

In Situ Treatment

- SERDP initiated bioremediation R&D in 1998
  - Fundamental and applied studies
  - Showed potential and method for cost effective treatment
  - Investment completed

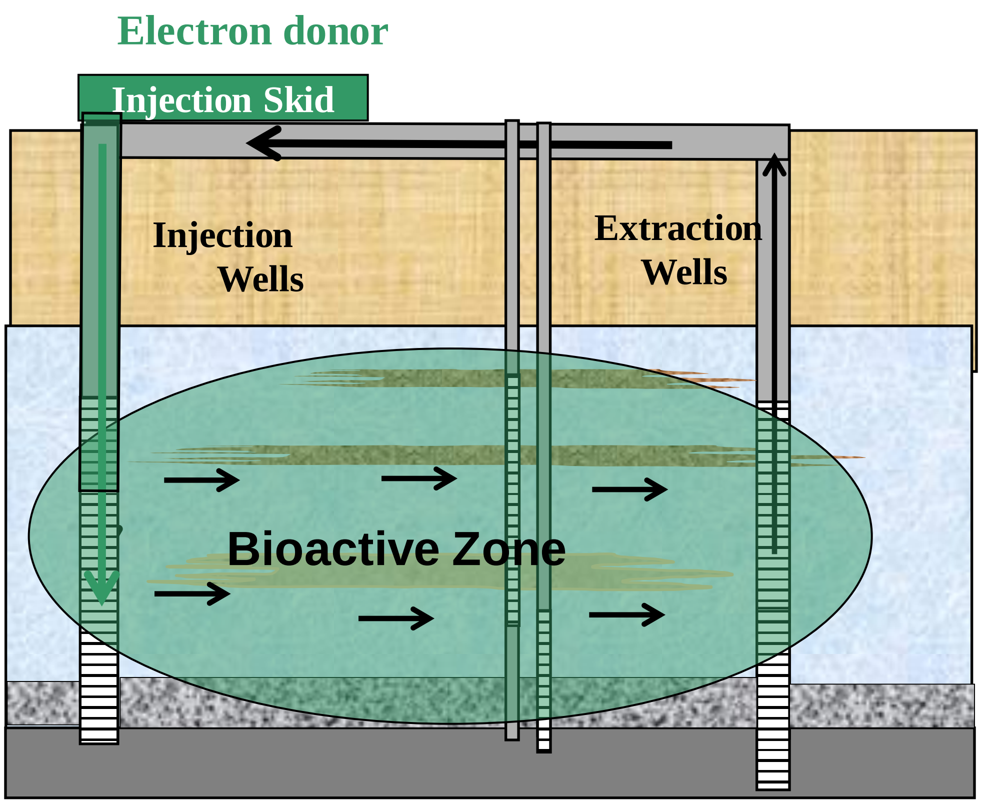
- Dozens of field demonstrations ongoing across DoD

- Fully commercialized
  - Two full-scale applications



Microbial Biodegradation of Perchlorate

Treatment Approaches

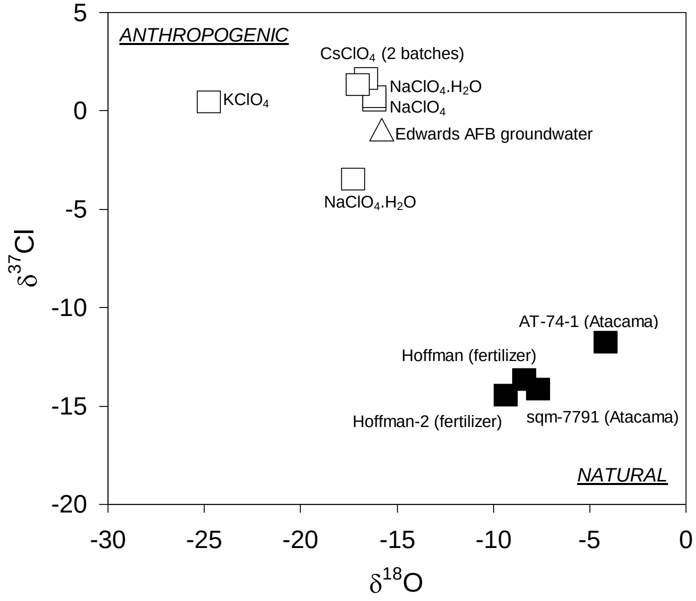


- **Active Treatment**
  - Soluble Electron Donor
  - Continuous pumping
- **Semi-Passive Treatment**
  - Soluble Electron Donor
  - Intermittent Pumping
- **Passive Treatment**
  - Slow Release Electron Donor
  - No Pumping

Considerations:
Mixing, O&M Costs, Biofouling, Secondary Groundwater impacts

Perchlorate Sources

- DoD Sources
  - Manufacturing
  - Demilitarization
  - Test and Training Ranges
- Natural Sources (FY05 Start)
  - Cause
  - Distribution
  - Fate
  - Identification
- Non Military Sources (FY05 Start)
  - Magnitude
  - Extent
  - Identification



Isotopic Identification of Perchlorate Sources

Road Flares

- **Background**
  - 20-40 million flares sold annually
- **Laboratory**
  - Lab studies showed 5-6% potassium perchlorate in unburned flares (10g for a 15 min flare)
  - Complete burning reduced perchlorate by 99% - still have up to 66 mg perchlorate in flare residue
- **Field**
  - Monitoring of background levels of perchlorate in highway runoff
  - Monitored highway run-off near a road flare deployed by State Police at an accident scene (I-95 MA)
  - Max $ClO4^-$ concentration leaving highway: ~ 314,000 PPB
  - Peak load of $ClO4^-$ leaving highway : 32.4 mg/min.
  - Total $ClO4^-$ load to receiving waters :1.3 g
  - Flares can be a significant point source of perchlorate

Fireworks

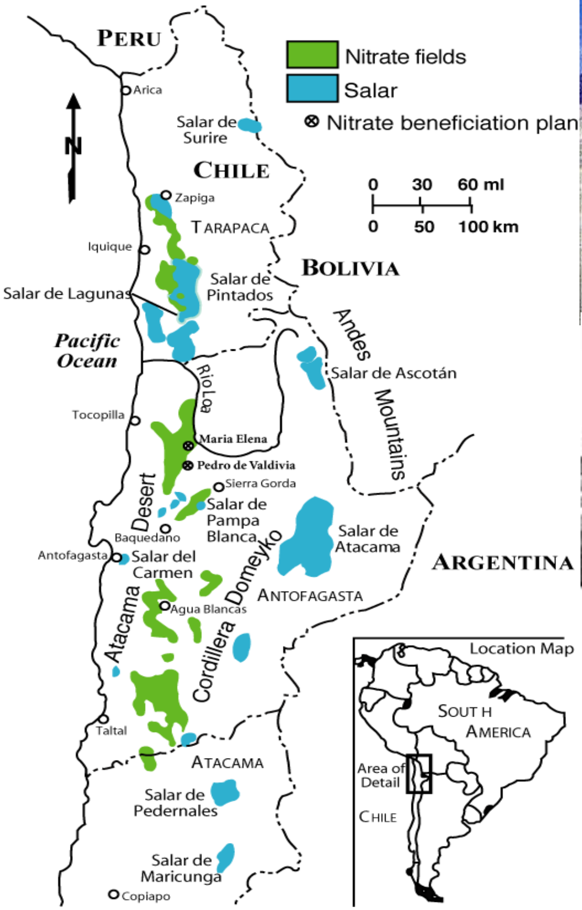
- Background
  - 221 million pounds consumed in U.S. in 2003
  - May contain up to 70 wt% potassium perchlorate
  - Case studies discussing contamination at display sites are limited
- Field Study
  - Concentration of perchlorate increased from ND to 5 mg/kg after firework display

Perchlorate and Metals Concentrations in Firework Charges

Parameter (mg/kg)	Charge 1	Charge 2
Perchlorate	389,000,000	355,000,000
Aluminum	77,000	120,000
Antimony	ND	ND
Barium	440	190
Calcium	1,700	720
Magnesium	80,000	120,000
Potassium	160,000	160,000
Sodium	ND	150
Strontium	18	22

- Perchlorate concentration in fireworks charge was 389 g/kg. Aluminum, magnesium and potassium were also present at high concentrations

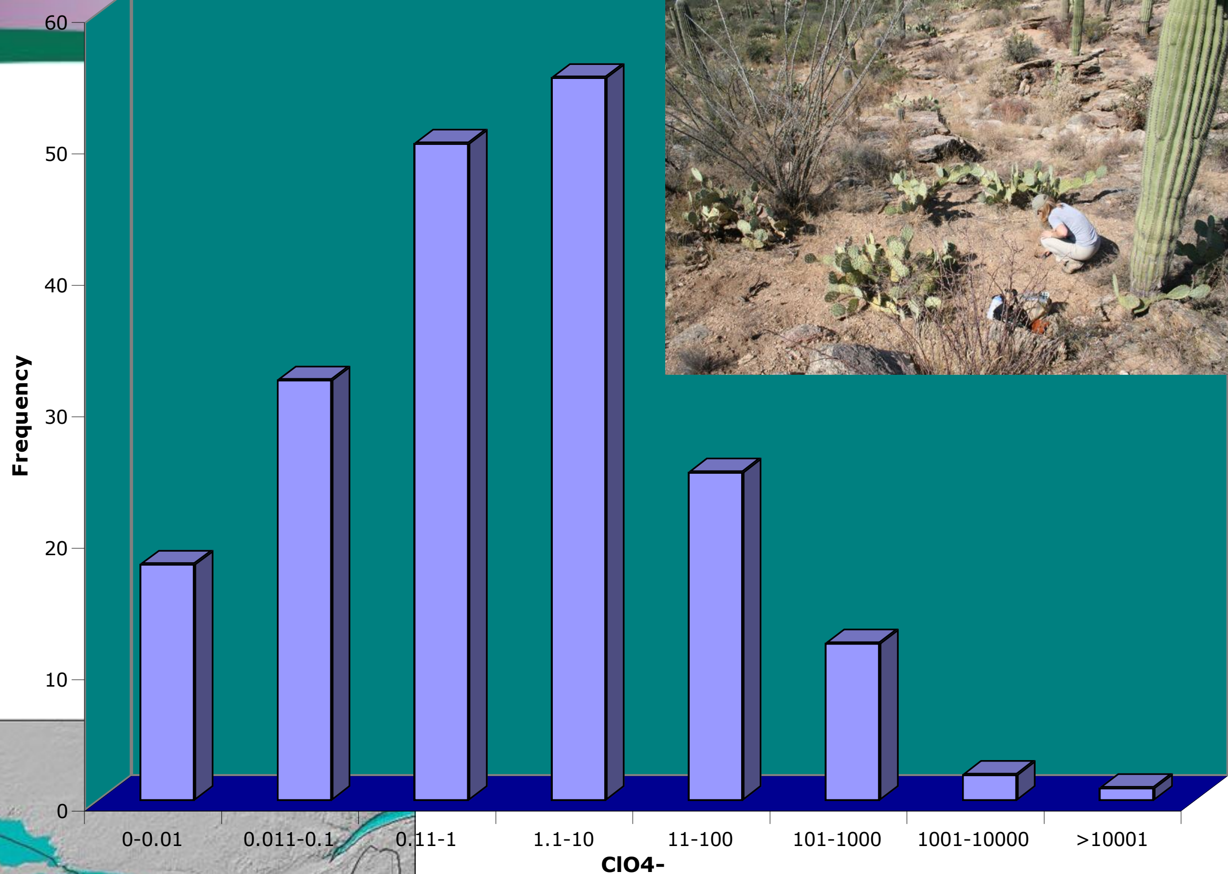
Natural Sources: Where it all started

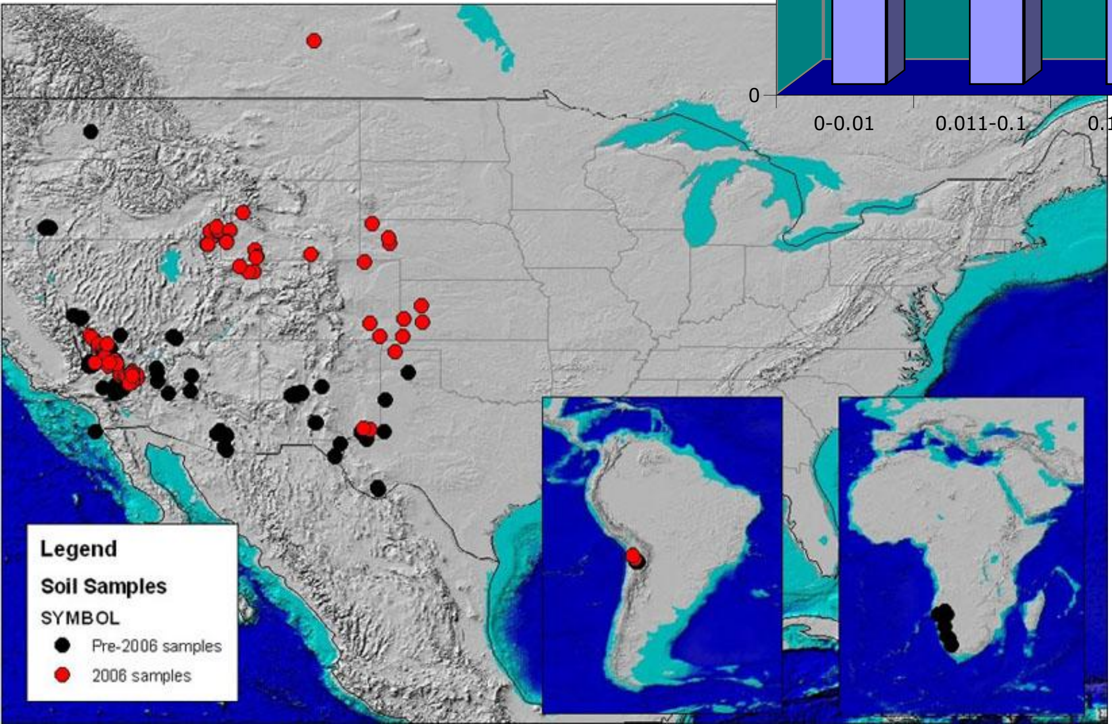


Chilean NO_3^- Deposits (Atacama Desert)

- Desert for at least last 1 MY
- ClO_4^- (>.1%) identified over 100 years ago
- Deposits also contain IO_3, CrO_7 (mg/kg in some strata)

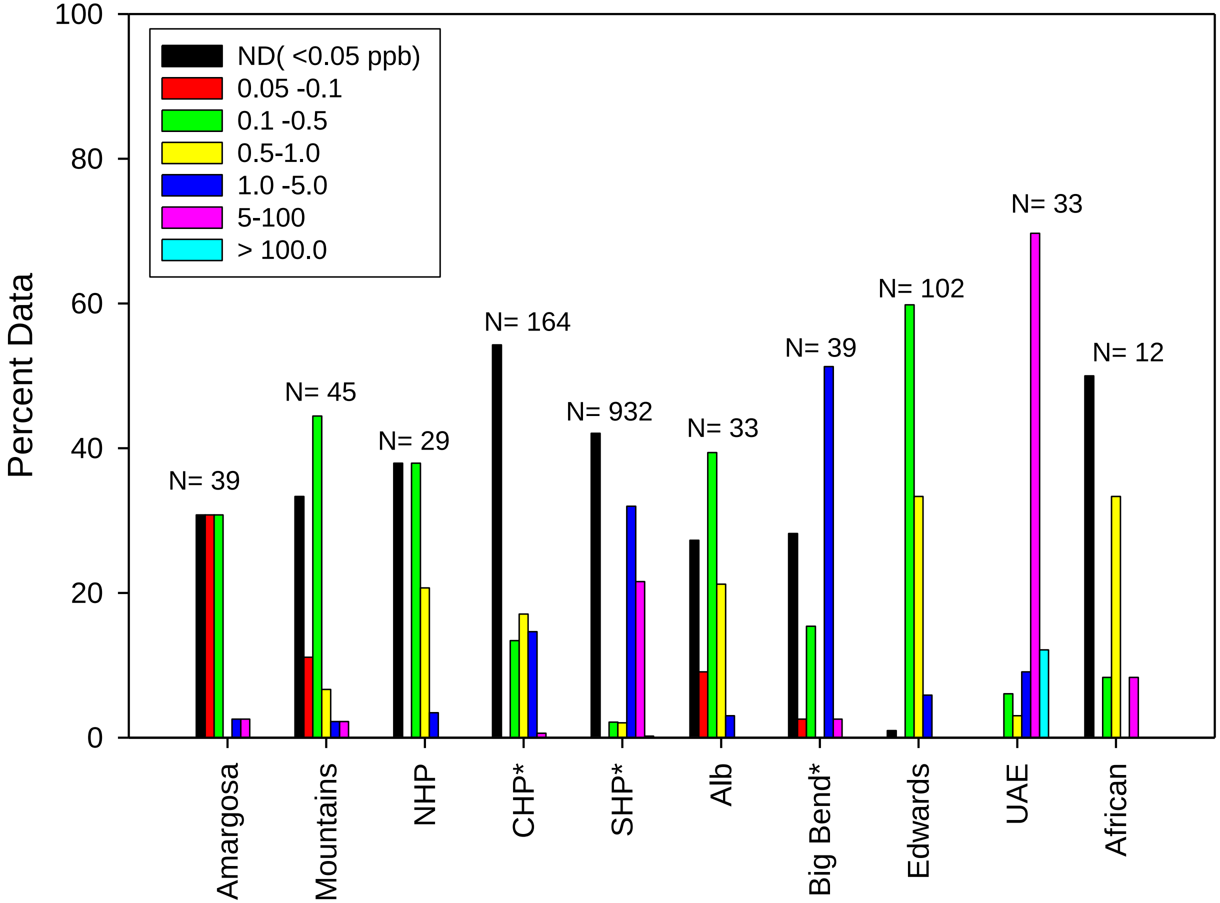
Does Natural Perchlorate Impact other Areas?



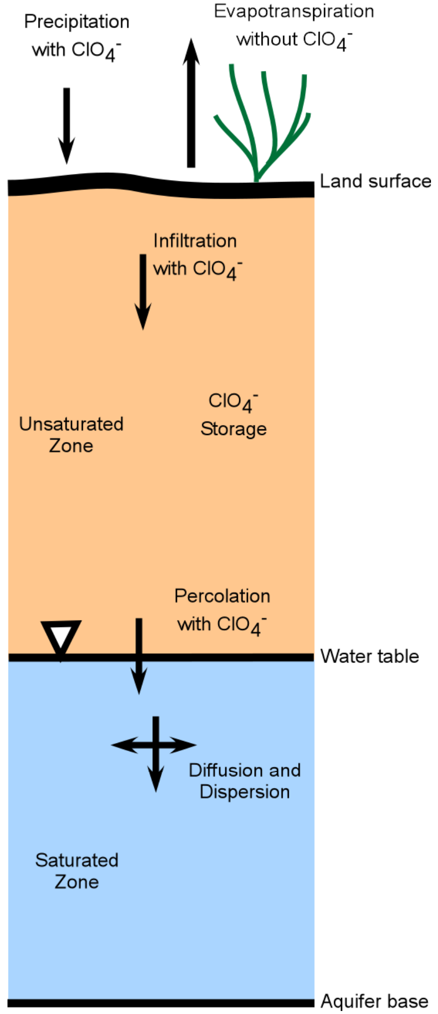


Concentration (ppb) Distribution of Perchlorate in Surface Soils

ClO_4^- Concentration Distribution in Groundwater from Selected Areas

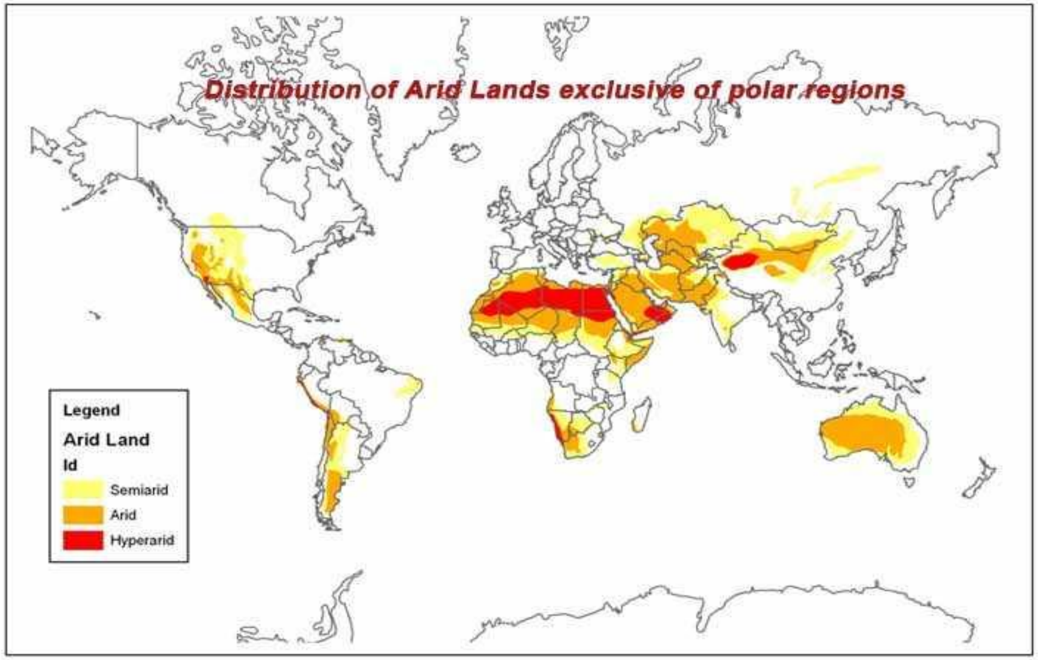


Proposed Perchlorate Accumulation Mechanisms



- Atmospheric Production and Deposition
- Partial Transport in Undisturbed Arid Areas
- Accumulation over long Periods
- Flushing Possible from Irrigation or Climate Shifts
- Not Stable in Anaerobic Environments and Some Plant Uptake

What's the Overall Significance?



- Exposure
  - Plants?
  - Milk?
  - GW?
- Future GW impacts
  - Desert Urbanization
  - Climate Change
  - Irrigation
- Site Assessment
  - Establish Background
  - Isotopic Differentiation

Natural vs. Anthropogenic Perchlorate

Key Question: Can You Distinguish Natural from Man-Made Perchlorate?

??

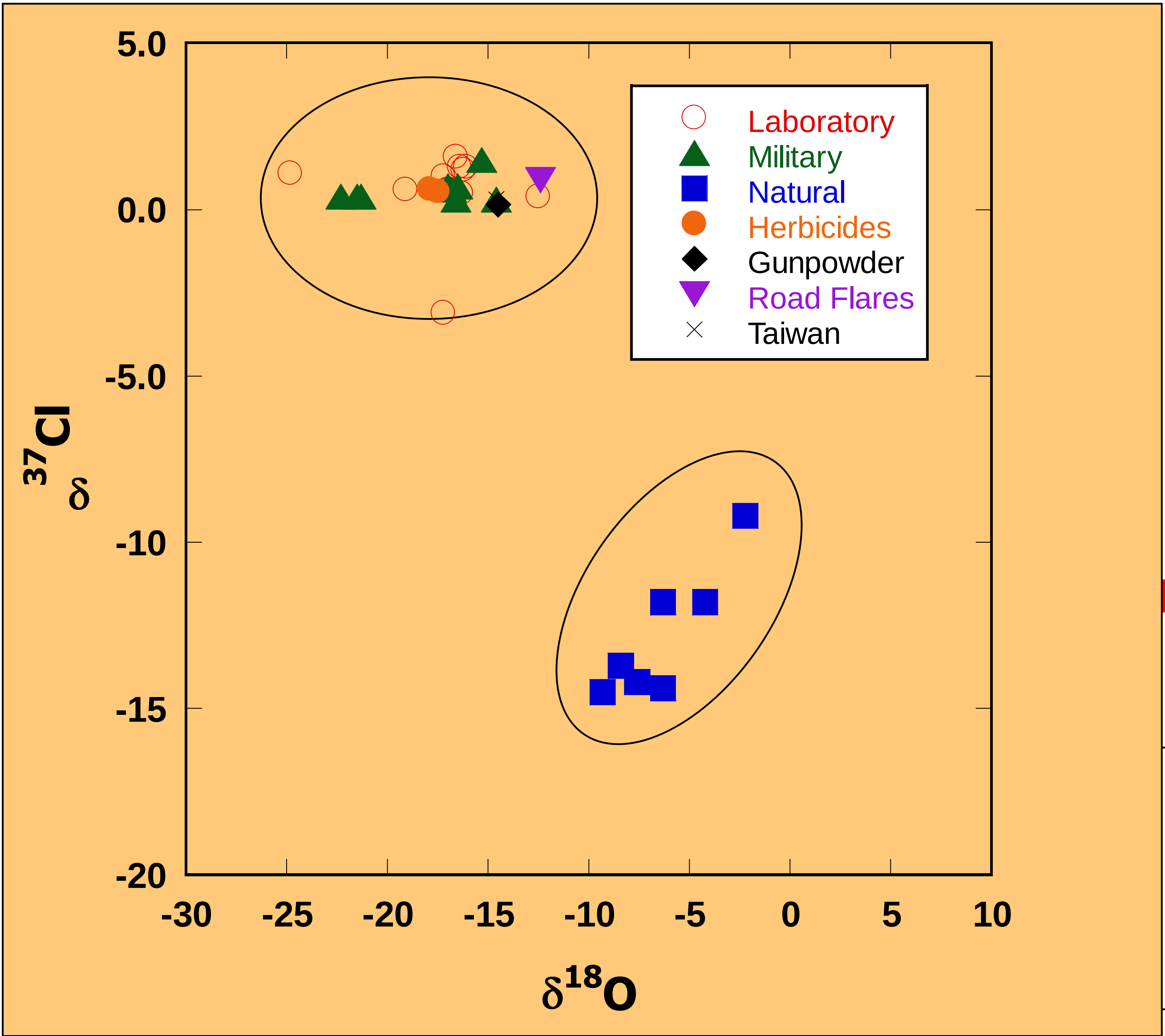
Isotope Ratio Analysis to Differentiate Perchlorate Sources

- Objectives
  - Analyze Isotope Ratios in Commercial, Military, and Natural Perchlorate Sources.
    - Develop broad database quantifying difference between natural and anthropogenic perchlorate.
  - Analyze Isotope Ratios of Perchlorate in Groundwater Plumes with Anthropogenic Origin and Suspected Natural Sources.
    - Demonstrate/validate isotopic procedure for forensic analysis.
- Elements in a compound can have widely different isotopic ratios based on mode of formation (e.g., ^{18}O in NO_3 from nitrification vs. atmospheric).
- Stable isotope ratios provide a unique “fingerprint” of a chemical compound, another dimension of information invisible from dissolved concentrations.

First Objective: Analyze Isotope Ratios in Commercial, Military, & Natural Perchlorate Sources

- Military sources
  - Propellant-grade perchlorate
  - Demilitarization activities
- Commercial sources
  - Reagent grade perchlorate
  - Fireworks
  - Emergency flares
  - Cotton defoliants
  - Bleach
- Natural sources
  - Chilean caliche
  - Natural fertilizers with Chilean nitrate
  - Southwest US: Evaporites
  - Potash salt

Results: Forensic Isotopic Analysis of Perchlorate δ³⁷Cl and δ¹⁸O



Chlorine markedly "heavier" in anthropogeni Perchlorate (n = 25).

δ^{37}Cl: **0.6 ± 0.9**
Range: - 3.1 to 1.6

δ^{18}O: **-17.2 ± 2.8**
Range: -24.8 to -12.5

Oxygen consistently "heavier" in natural Perchlorate (n = 7).

δ^{37}Cl: **-12.8 ± 2.0**
Range: -14.5 to -9.2

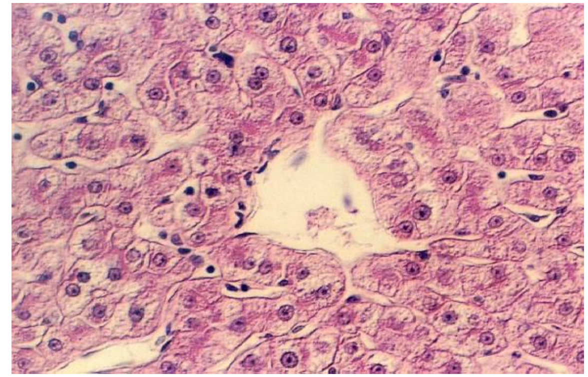
δ^{18}O: **-6.3 ± 2.5**
Range: -9.3 to -2.2

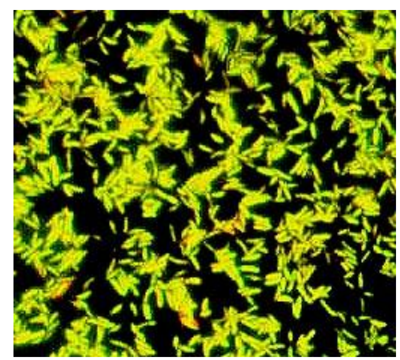
NDMA

- Toxicology
  - NDMA is a potent mutagen, teratogen, & carcinogen.
  - EPA 10^{-6} Lifetime Cancer Risk = 0.7 ng/L.
  - California DHS; 10 ng/L Action Level;
    California OEEHA 3 ng/L PHG (12/2006)
- Sources
  - 1,1-Dimethylhydrazine Rocket Fuel[$(CH_3)_2NNH_2$]
  - Aerozine 50 (Mixture of Hydrazine and 1,1DMH)
  - Disinfection Byproduct (Chloramine)
  - Industrial, Agricultural and Food Sources.
- Treatment
  - Pump-and-Treat with UV Irradiation
  - 1000 mj/cm^2 for 10-fold reduction
  - (10X for *Cryptosporidium*)

Biological Degradation of NDMA

- Summary of Previous Research:
  - **Mammalian Metabolism**
    - Cytochrome P-450 System
  - **Biological Degradation**
    - Several Papers 1970's – 1980's
    - Biodegradation Observed in Soils and Lake Water, Intestinal Bacteria
    - Persistent in Groundwater
  - **No Environmental Isolates Capable of Growth on NDMA**
  - **One Isolate Capable of Cometabolism**
    - *Methylosinus trichosporium* OB3b





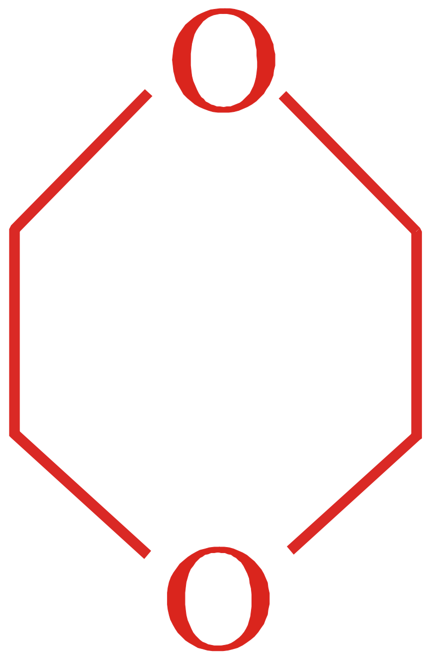
Potential Remedial Applications

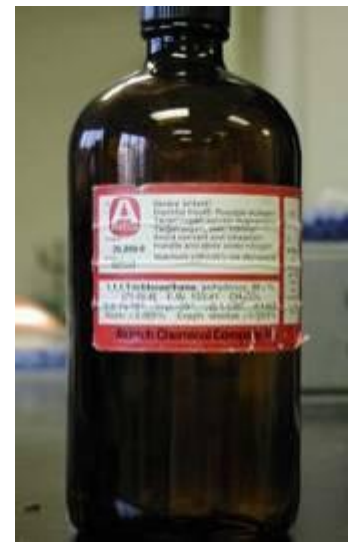
NDMA Summary

- Treatable by UV Oxidation
- *In Situ* and *Ex Situ* Biotreatment Possible
  - May require propane biostimulation to reach low levels
- *Ex Situ* Metal Catalyst Treatment Showing Promise (*Data not shown*)

1,4-Dioxane

1,4-Dioxane





1,1,1-Trichloroethane

The 1,4-Dioxane Problem

- Used extensively as a stabilizer in chlorinated solvents
  - Primarily used with 1,1,1-TCA
  - 1,1,1-TCA found at 809 NPL sites (www.atsdr.gov; 2004)
- 1,4-Dioxane has recently emerged as a contaminant of concern
  - Low action levels in several states: California (3 ppb); Florida (5ppb); Maine (70 ppb); Massachusetts (50 ppb); Michigan (1 ppb); North Carolina (7ppb)
  - Risk of closed sites being re-opened
- Little detailed information on the fate of 1,4-dioxane in groundwater
  - Few biodegradation studies

Current Treatment Options for 1,4-Dioxane

- *In situ* oxidation
  - Reported to work in some cases
- Advanced Oxidation (HiPOx)
  - Some full-scale systems in place
- Biological Treatment
  - Co-metabolic process (propane/THF)
  - Biological treatment has proven to be challenging
- No universal solution yet available

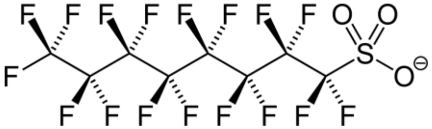
Perfluoroalkyl Contaminated Groundwater

- FY11 SON: In Situ Remediation of Perfluoroalkyl Contaminated Groundwater
- Objectives:
  - Improve understanding of mechanisms involved in F&T processes in groundwater under varying natural & engineered conditions.
  - Determine impact of co-contaminants on F&T processes.
  - Improve understanding of behavior of perfluoroalkyl contaminants under typical remedial technologies for co-contaminants.
  - Develop remedial strategies for perfluororalkyl contaminants, including consideration of the necessity for treatment train approaches to facilitate treatment of co-contaminants.

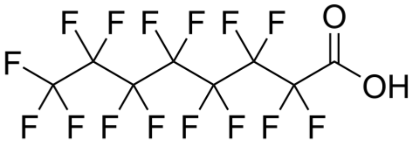
What Are Perfluorochemicals (PFCs)?

- General formula: $F(CF_2)_n{-}R$
  - Hydrophobic alkyl chain of varying length (typically C_4 to C_{16})
  - Hydrophilic end group
- Man-made compounds with unique chemical properties
  - Very stable and persistent in the environment
  - Ionic form of PFCs – highly soluble, non-volatile, and poorly sorb to soil
- Primary PFCs of interest
  - Perfluorooctane sulfonate (PFOS)
  - Perfluorooctanoic acid (PFOA)

$C_8HF_{17}O_3S$



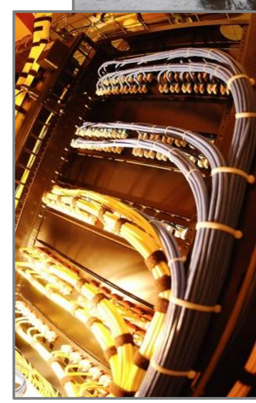
$C_8HF_{15}O_2$



What Are PFCs Used For?

- Used to make:
  - Fluoropolymer coatings and products that resist heat, oil, stains, and grease.
    - Clothing
    - Furniture
    - Food packaging
    - Heat resistant non-stick cooking surfaces
    - Electrical wire insulation
  - Fluorosurfactants
    - Aqueous film forming foam (AFFF)
    - Chromium plating mist suppressants
    - Stain repellants
    - Photolithographic chemicals



Aqueous Film Forming Foam

- AFFF
  - Developed in 1960s by 3M and U.S. Navy for use on Class B fires (flammable liquids)
  - Contains fluorosurfactants other compounds as required) per MILSPEC MIL-F-24385F(SH)
  - Low surface tension and positive spreading coefficient enable film formation on top of lighter
- PFCs in AFFF
  - Historically, AFFF contained PFOS and small percentage of PFO (disassociated form of PFOA)
  - 3M, sole producer of PFOS in the U.S., discontinued production of PFOS in 2001
  - Continued use of stockpiled PFOS-based AFFF not currently restricted under U.S. regulations
  - AFFF now produced using smaller chain PFCs $(<C_6)$ fuels

Growing Regulatory Interest in PFCs

- Interest driven by findings of PFCs in :
  - Occurrence in biological organisms and environmental media
  - Groundwater near PFC manufacturing and disposal facilities
    - DuPont Washington Works Facility, West Virginia
    - 3M Cottage Grove Facility, Minnesota
    - Numerous landfills and disposal sites in Minnesota
  - Soil and groundwater near fire training facilities in Minnesota
  - Soil and compost at north Georgia wastewater treatment facility
  - Sewage sludge and agricultural soils in Alabama
  - Public water supply systems in New Jersey

Federal Regulation Related to Cleanup

- CERCLA - not a hazardous substance, pollutant, or contaminant
- Not RCRA regulated waste (listed or characteristic)
- PFOA/PFOS not currently regulated under the USEPA Safe Drinking Water Act
  - Recently included on the USEPA Drinking Water Contaminant Candidate List (CCL3)
- USEPA Provisional Health Advisory Values
  - PFOA – 0.4 µg/L
  - PFOS – 0.2 µg/L
  - Developed in response to contaminated agricultural sites in Alabama but values can be used to assess exposure at other sites
  - Based on
    - 10-kg child consuming 1 L drinking water per day.
    - Default relative source contribution (RSC) – 20%

State Environmental Guidelines/Action Levels

Guideline / Action Level	Media	PFOA	PFOS
Minnesota Health Risk Limit	Groundwater	0.3 µg/L	0.3 µg/L
North Carolina Interim Maximum Allowable Concentration	Groundwater	2 µg/L	-----
New Jersey Preliminary Guidance Value	Drinking Water	0.04 µg/L	-----
California – under review for possible Prop. 65 listing	NA	√	-----
Washington Persistent Bioaccumulative Toxins Rule	NA	-----	√

Environmental release of PFCs

- Historical testing or emergency activation of fire suppression systems in hangars
- Leaks from storage tanks and pipelines
- Historical fire fighter training exercises

Scope

- Scope of potential impact difficult to define
- Site investigations have not typically included analysis for PFCs, given their emerging status
- Scope of potential problem can be estimated using the number of “Fire/Crash/Training” sites as a surrogate for actual site data
  - May underestimate problem by not including AFFF spills, pipeline leaks, or testing/emergency activation of aircraft hangar fire suppression systems

Potential Impacts to DoD Restoration Program

DoD Fire/Crash/Training Sites

Service	Total Sites	Remedy in Place (RIP)		Response Complete (RC)	
		RIP ≤ 2008	RIP > 2009	RC ≤ 2008	RC > 2009
Air Force	***353***	***296***	***47***	***249***	***104***
Army	94	7	6	79	15
Navy	132	115	17	51	56
DLA	3	1		3	
FUDS	12		1	7	5
Total	***594***	***419***	***71***	***389***	***180***

Data obtained from the DoD Knowledge Based Corporate Reporting System (KBCRS), 2008

Cleanup Challenges

- Many conventional treatment approaches are not effective for PFCs in water (e.g., direct oxidation, air stripping, vapor extraction)
- Technologies currently available to treat PFCs in water include
  - Granular activated carbon (GAC) is most effective method
    - Drinking water treatment (municipal and private wells)
    - Landfill water treatment
  - Reverse osmosis is effective for higher concentration industrial waste streams
- Bench-scale research to develop alterative treatment approaches continues

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